

# Synthesis, Photochromic Property and Application for Optical Recording of a New Asymmetrical Diarylethene

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Received October 26, 2012; revised November 27, 2012; accepted December 14, 2012

## ABSTRACT

The reversible molecule switching of an asymmetrical photochromic diarylethene 1-[2-methyl-5-(3-chlorophenyl)-3-thienyl]-2-(1,2-dimethyl-3-indol) perfluorocyclopentene (**1a**) has been prepared for the examination of photo-switching, fluorescence switching. This compound exhibited reversible photochromism, changing from colorless to blue after irradiation with UV light both in solution and in poly-methyl methacrylate (PMMA) amorphous film. Also, it exhibited remarkable fluorescence switching in the solid state. Using diarylethene **1b**/PMMA film as recording medium, polarization optical recording was performed perfectly by a He-Ne laser with 633 nm wavelength. The results demonstrated that it can be potentially used as polarization optical recording medium.

**Keywords:** Diarylethene; Fluorescence; Optical Recording

## 1. Introduction

Photochromic materials have been extensively investigated for their potential applications in erasable optical memories, displays, and optical switches [1]. The properties of photochromic materials, such as their absorption spectrum, refractive index, dielectric constant, oxidation and reduction potentials, photoluminescence, dipole moment, and ionization potential (Ip), can be changed reversibly during the photochromic process. This unique character can be applied to different types of photonic devices [2-5]. Among the photochromic compounds, diarylethenes are regarded as the best candidates for such devices [1], because of their advantages such as a high efficiency of photoisomerizations, sufficient thermal stability of both the open and the close forms, a very high resistance to photofatigue, and the ease with which the reaction can be monitored by UV-vis spectroscopy [6-9]. These differences have been utilized to control their functions such as electrical conductivity, alignment of liquid crystals, light-driven organogelators, and photo-controlled release and uptake.

Among diarylethene derivatives so far synthesized [10-13], most of the heteroaryl moieties have been thiophene or benzothiophene rings, and other heteroaryl

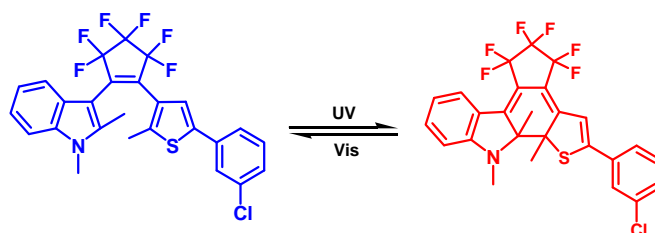
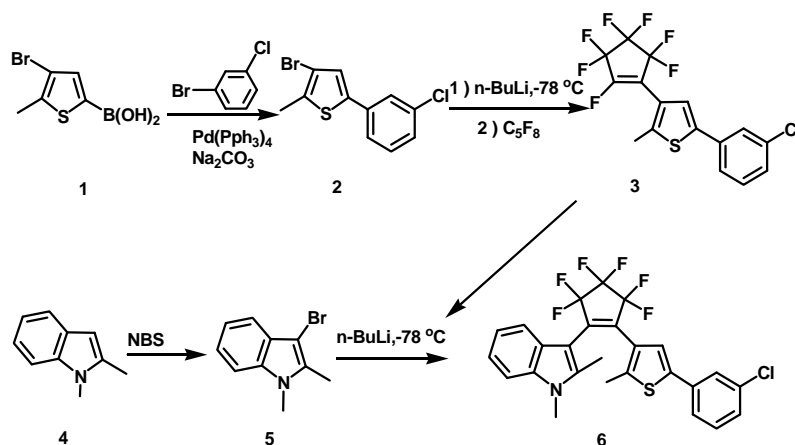
moieties, such as furan, thiazole, benzofuran, pyrrole and indene [1], have also been reported partially. But diarylethene bearing thiophene and indole moieties haven't been reported until now. In this paper, we have designed and prepared a new asymmetrical diarylethene derivative with thiophene and indole moieties. *i.e.*, 1-[2-methyl-5-(3-chlorophenyl)-3-thienyl]-2-(1,2-dimethyl-3-indol) perfluorocyclopentene (**1a**).

We synthesized asymmetrical diarylethenes having an indole moiety, and the compound showed good thermal stability and strong fatigue resistance in the solid state. The results that asymmetrical diarylethene with an indole moieties have better thermal stability and stronger fatigue resistance than the symmetrical one are very interesting and important. Its photochromic reactivity, fluorescence property and application for optical recording were investigated. The photochromic reaction of diarylethene **1a** is shown in **Scheme 1**.

## 2. Experimental

The synthetic route for diarylethene **1a** is shown in **Scheme 2**. It was synthesized according to the similar procedure of Pu *et al.* [12]. The structure of compound **1a** was confirmed by <sup>1</sup>H NMR spectroscopy, IR and <sup>13</sup>C NMR spectroscopy. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ1.80 (s, 3H, -CH<sub>3</sub>), 2.04 (s, 3H, -CH<sub>3</sub>), 3.65 (s, 3H, -CH<sub>3</sub>),

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Scheme 1. Photochromism of diarylethenes **1a**.Scheme 2. Synthetic route for the compound **1a**.

7.14 (t, 1H,  $J = 8.0$  Hz, thiophene-H), 7.22 (d, 1H,  $J = 8.0$  Hz, phenyl-H), 7.29 (d, 1H,  $J = 8.0$  Hz, phenyl-H), 7.39 (s, 1H, phenyl-H), 7.48 (t, 1H,  $J = 8.0$  Hz, phenyl-H), 7.56 (t, 2H,  $J = 7.6$  Hz, phenyl-H), 7.74 (t, 2H,  $J = 8.0$  Hz, phenyl-H);  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  11.46, 14.21, 30.01, 109.21, 113.37, 116.50, 118.38, 119.50, 122.14, 124.42, 125.57, 127.17, 128.90, 129.59, 129.84, 130.81, 134.89, 137.13, 138.82, 142.35; IR (KBr,  $\text{cm}^{-1}$ ): 752, 779, 812, 840, 869, 893, 972, 997, 1020, 1047, 1078, 1112, 1161, 1182, 1276, 1340, 1400, 1458, 1624, 1668, 3170. Calcd for  $\text{C}_{26}\text{H}_{19}\text{ClF}_6\text{NS}$  (%): Calcd C, 59.38; H, 3.45; Cl, 6.74; N, 2.66; S, 6.10. Found C, 59.13; H, 3.34; Cl, 6.80; N, 2.74; S, 6.24; mp: 143.5°C - 145.3°C.

The recording film was prepared as follows: diarylethene **1a** (10 mg) was dissolved ultrasonically in PMMA-chloroform solution (10%, w/w, 1 ml). The mixture solution was then spin coated on a glass substrate (20 mm  $\times$  20 mm  $\times$  1 mm) which was then dried in air at room temperature. The thickness of the film was about 12  $\mu\text{m}$ . The sample was colored homogeneously by irradiation with 313 nm UV light to convert the open-ring isomer (**1a**) to the closed-ring isomer (**1b**) before being recorded.

### 3. Results and Discussion

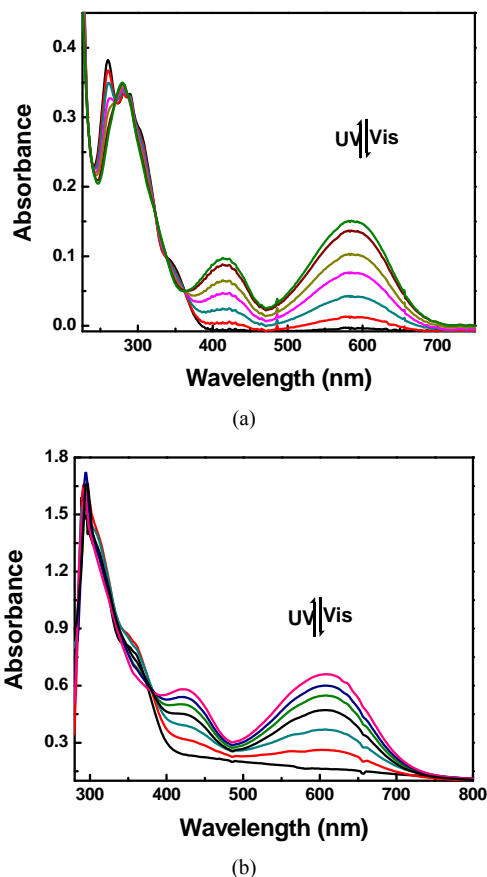
#### 3.1. Photochromism of Diarylethene

The diarylethene **1a** exhibits good photochromism both in hexane solution ( $2 \times 10^{-5}$  mol·L $^{-1}$ ) and in PMMA

amorphous film (10% w/w). As shown in **Figure 1**, in hexane solution, the absorption maximum of compound **1a** was observed at 220 nm ( $\epsilon = 5.5 \times 10^4$  L·mol $^{-1}$ ·cm $^{-1}$ ). Upon irradiation with 313 nm light, the colorless solution of **1a** turned blue, in which the absorption maximum was observed at 557 nm ( $\epsilon = 8.9 \times 10^3$  L·mol $^{-1}$ ·cm $^{-1}$ ). Correspondingly, the blue colored solution returned to colorless upon irradiation with visible light ( $\lambda > 500$  nm), indicating that **1b** returned to the initial open-ring isomer **1a**. Similarly, upon irradiation 313 nm light, the color of dithienylethene **1b**/PMMA film ( $\lambda_{\text{max}} = 275$  nm) changed from colorless to blue with the appearance of a new broad absorption band at  $\lambda_{\text{max}} = 575$  nm, which was assigned to the formation of the closed form **1b**. The red shift of the ring-closed form of diarylethene **1** in PMMA film in comparison with that in hexane solution can be ascribed to the stabilization of molecular arrangement in solid state.

#### 3.2. Fluorescence of Diarylethene **1a**

The fluorescence properties in hexane and in PMMA amorphous film of the compound **1a** were measured using a Hitachi F-4500 spectrophotometer, and the breadths of excitation and emission slit were selected 10.0 nm and 20.0 nm, respectively. As shown in **Figure 2**, the fluorescence intensity of diarylethene **1a** decreased dramatically along with the photochromism from open-ring isomer to closed-ring isomer upon irradiation with 313 nm

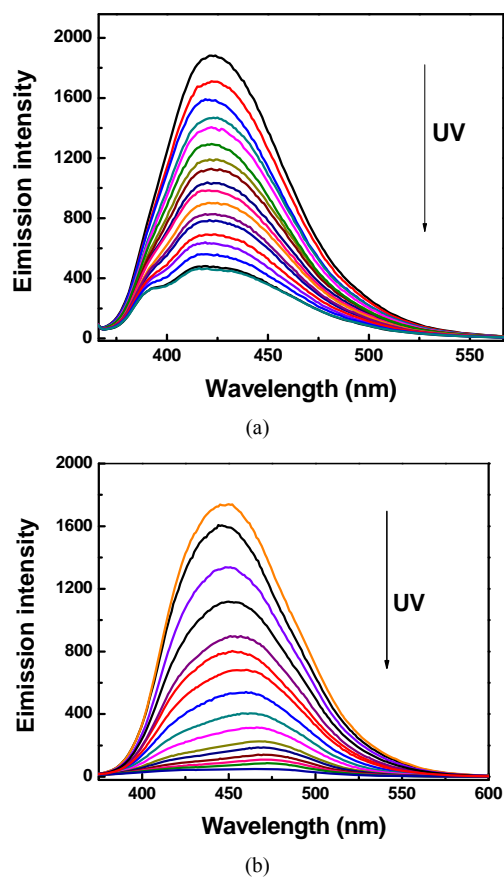


**Figure 1.** Absorption spectral changes of diarylethene **1** both in hexane and in PMMA film at room temperature: (a) in hexane ( $c = 2.0 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ ); (b) in PMMA film (10%, w/w).

light in hexane and in PMMA film. When irradiated by light of 313 nm, the photocyclization reaction was carried out and the non-fluorescent closed-ring form of the compound was produced. The hexane solution and the PMMA film of **1a** exhibited relatively strong fluorescence at 421 and 453 nm when excited at 355 nm. The back irradiation by appropriate wavelength visible light regenerated its open-ring isomer and recovered the original emission intensity.

### 3.3. Optical Storage

The evaluation of potential of photochromic material as an erasable storage medium by recording, reading and erasing the optical image in a real-time operation was investigated. For the sake of long-term stability and environmental durability of storage devices, photoresponsive materials must be processed into large-area, high quality solid films. Usually, photochromic materials are doped into a polymer matrix for investigation of applications, and PMMA was chosen in this paper to be used as polymer matrix for optical recording. Using dithieny-

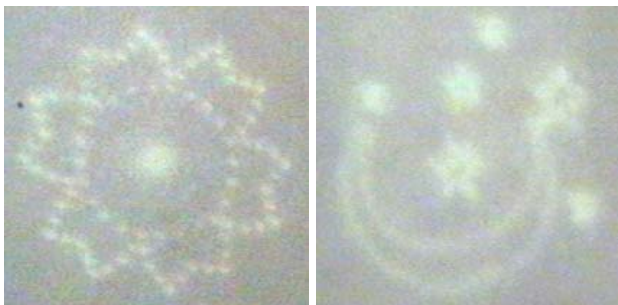


**Figure 2.** Fluorescent intensity changes of diarylethene **1**(a) in hexane and (b) in PMMA film.

lene **1c**/PMMA as the recording medium, optical storage was performed by a 650 nm He-Ne laser. The film was colored homo-geneously by irradiation with UV light before optical recording. With a He-Ne laser in the experimental setup, the exposure time for each spot was 0.08 s and the patterns were about 20  $\mu\text{m}$ . The polarizations of the patterns recorded on dithienylethene **1b**/PMMA film is shown in **Figure 3**. The result indicated that the new photochromic diarylethene can be applied in high capacity optical storage. As shown in **Figure 3**, the quality of optical recorded in **1c**/PMMA film is also fairly good.

### 4. Conclusion

A novel photochromic diarylethene **1a** was synthesized and its photochromic, reaction kinetics and fluorescent properties were investigated. The results showed that this compound exhibited good reversible photochromism both in solution and in PMMA amorphous film. It also exhibited remarkable fluorescence switching. Using diarylethene **1b**/PMMA as recording medium, the results demonstrated that the diarylethene compound had attractive properties for high capacity optical storage.



**Figure 3.** Readout patterns from the diarylethene 1c/PMMA film.

## 5. Acknowledgements

A project supported by scientific research fund of Sichuan Provincial Education Department (10ZC063, 10ZC064, 12ZA146, 12ZB118).

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